MODIFIED HZSM-5 AND H-MORDENITE ZEOLITES AS SUPPORTS FOR PLATINUM CATALYST

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ABSTRACT

Bifunctional Pt/HZSM-5 and Pt/HMOR catalysts were prepared and applied to the isomerization of n-Hexane. Catalysts containing 0.3wt% Pt on both catalysts with potentially high acidity were prepared by impregnation method. The tested catalysts show that optimum selectivity with maximal isomer yield was obtained for Pt/HZSM-5 catalysts. The nanoparticles were characterized by inductively coupled Plasma (ICP), X-Ray Diffraction (XRD), BET Surface Area, and Transmission Electron Microscopy (TEM). TEM was revealed uniformly dispersed platinum particles on the substrate with average particle size ranging from ~6.893 to 8.847nm. It was demonstrated that the loading content and particle size of the nanoparticles deposited on zeolites could be tuned by changing the weight of precursor and the conditions of loading.

Keywords: *Isomerization: n-Hexane: Impregnation: Zeolite: Platinum: H-ZSM-5: H-MOR*

1.INTRODUCTION

High environmental standards have eliminated the usage of the lead-based additives for busting the octane number (ON) in gasoline in the most of developed countries. In addition to environmental concern this process was speed up by the fact that three-way catalysts were poisoned by lead additives. The elimination of these additives brought about the problem of gasoline blending in order to reach the high ON. The new restrictions towards aromatics content in gasoline (reformulated gasoline) [1,2], have further tight the ON issue. Boosting gasoline with oxygenates, MTB, e.g., turned out to be limited due to shortage of MTB [2]. Besides, it was found that gasoline containing extra oxygen suffers from a loss in fuel economy [3]. The answer might be in hydroisomerization of straight C5–C6 paraffins to corresponding isomers, particularly when combined with adsorption of left-over *n*-paraffins in product [1]. Isomerization reactions of alkanes require a bifunctional catalyst and can be achieved on Cl–Al2O3-type catalyst containing a noble metal [4]. However, due to sensitivity to trace impurities in feed such as water, these catalysts are being replaced by zeolite-based catalysts. Zeolites like MFI [5], L [6–8], mordenite [5,9,10], Y [5,6,11,12], with or without incorporated noble metals, have been investigated. The results indicate the importance of metal loading, acidity of the support, as well as properly balanced metallic and acidic functions.

In this study, Zeolite ZSM-5 and Mordenite have been used to prepare platinum-incorporated zeolite by the Impregnation method using Hexachloroplatinic acid, (H_2PtCl_6). After adsorption on to the Zeolite, the precursor was reduced, resulting in zeolites-supported Pt nanoparticles with slightly uniform size distribution. The morphology of these supported metal nanocomposites were characterized by inductively coupled Plasma (ICP), X-Ray Diffraction (XRD), BET Surface Area, Transmission Electron Microscopy (TEM) and Thermo Gravimetric Analysis (TGA).

2. EXPERIMENTAL WORK

2.1 Materials

Two types of zeolite have been used namely ZSM-5 and Mordenite contains hydrogen cation HZSM-5 and HMOR with Si/Al=90 and 40 respectively were donated from Sud-Chemi company. H_2PtCl_6 was purchased from Strem Chemical. All of the chemicals were used as received except for zeolites, where it was dried using heat gun under vacuum to remove all moisture from the pores.

2.2 Loading of Platinum Metal

The experimental work was done in the Institute for Technical Chemistry and Macromolecular Chemistry (ITMC/ RWTH University/ Aachen/ Germany). To produce 0.3 wt % of Platinum on the supports by impregnation. 125 mg of H_2PtCl_6 and 8 g of each zeolites have been used in each experiment. The zeolite sample was put in a conical flask with 20ml distilled water followed by addition of H_2PtCl_6. Since, the Hexachloroplatinic acid is easy soluble in water producing a yellow to orange solution. The closed flask solution was mixed at room temperature for 24 hr. It was observed that after about five hour of mixing, the color of solution was disappeared, indicating that the most quantity of platinum complex was impregnated.

The loaded zeolites sample was filtered off and washed carefully with distilled water and then dried in an oven for 24 hr at 110 ^oC. The calcinations of catalyst samples was carried out in the reactor, at a temperature of 260 ^oC for 3 hr under dry air flow of 100 ml/min. The reduction of catalyst samples were also done in the reactor immediately after the calcination by hydrogen at 350 ^oC for about 3.30 hr.

2.3 Catalytic Characterization

The quantity of metal loaded to the zeolite was analyzed as discussed elsewhere [13]. Samples of supported platinum were digested with 5ml of HNO_3 and 5ml of HCl in a hot black tube at 95^{o}C for 4hr. After being kept at room temperature overnight, 2ml of HF was added to the sample solutions and digested at 95^{o}C for 2hr. The resulting solutions were analyzed by inductively coupled plasma spectroscopy (ICP) in the Institute of Fuel Chemistry and Physicochemical Process Engineering (IBC Inst. / RWTH University/ Aachen/ Germany).

X-Ray Diffraction spectra of the sample were recorded using Siemens D5000 (IBC Inst.) with a moving phase sensitive detector using CuK_α radiation (44 kV, 35 mA) over 2θ range of 3^o-$90^o$with step 1^oat residence time 5s at each point. The data was smoothed to increase the signal-to-noise ratio.

The BET surface areas were determined by adsorption and desorption data of liquid nitrogen acquired on a Micromeritics ASAP 2000 apparatus (IBC Inst.). The samples were evacuated under vacuum of $5*10^{-3}$ torr at 350°C for 15hr.

The morphology of the supported metal nanocomposites has been characterized by Transmission Electron Microscopy (TEM). The first step in the TEM preparation is a mechanical treatment of the materials, like sawing, ultra-sonic grinding or punching to give the sample a circular form with a diameter of approximately 3mm. To prepare cross-sectional specimens of, e.g., grain boundaries or heterophase interfaces, the formation of sandwiches of the film/substrate material is a common procedure, which is later on glued inside a ceramic or metallic tube. After sawing the tube in small disks, each disk is mechanically grinded to a thickness of 100 mm to 150 mm. In most cases, the grinding is followed by a dimpling process until the specimen thickness reaches 10 mm to 50 mm in the thinnest regions. The final thinning procedure is performed by Ar+ ion bombardment with ion energies in the range of 100eV to 6 keV. Within this preparation step the ion-thinning parameters, such as the glancing angle or the ion-beam energy are varied to obtain an optimal TEM specimen quality. An in-situ observation of the ion-thinning is possible since all ion-thinning machines are equipped with light microscopes and video cameras. These were examined in the Max Plank Institute (MPI/ Mulhaim). Chemical microanalysis was performed in Institute of Central Facility for Electron Microscopy (GFE/ RWTH Aachen) in situ using an EDAX Phoenix atmospheric thin-window energy-dispersive X-ray spectrometer (EDXS).

2.4 Reaction Experiment

The Pt over zeolite sample HZSM-5 and HMOR loaded by impregnation method were tested for isomerization of n-hexane. The setup of the apparatus used for reaction was shown in figure 1.

The samples were originally extruded (1.5mm*2-3mm), charged into the reactor and activated for one hour at temperature 350 C^o just before runs in flow of hydrogen, (100ml/min). 8g of each catalyst type was used in each run.

n-Hexane feed was charged to the pump from a reservoir. Feed was pumped under pressure and passed through one way valve to microstructure evaporator to heated up of n-hexane to about 150 C^o. Outlet from the evaporator was mixed with hydrogen before the reactor inlet then passed through the catalyst bed from the bottom of reactor.

The product was cooled with heat exchanger using cooled water (inlet temperature 5 C^o) then passed through digital back pressure regulator manufactured by (Burkert 8624-2) maximum operating pressure 28 bar. The product gas entered to the separator that filled with iso-propanol dry ice (T = -98 C^o). The uncondensed gas product connected online to GC, while condensed liquid samples was collected and analyzed with another GC.

A pre test period of about half hour was used before each run to adjust the feed rate and temperature to the desired values. The catalyst samples have been tested under a wide range of operating temperature 250-325 C^o. Hydrogen total pressure was kept constant at 5 bar, liquid hour space velocity (LHSV) equal to 1.76 hr^{-1} and hydrogen to hydrocarbon ratios (H_2/HC) were taken 3, 6 and 9 moles.

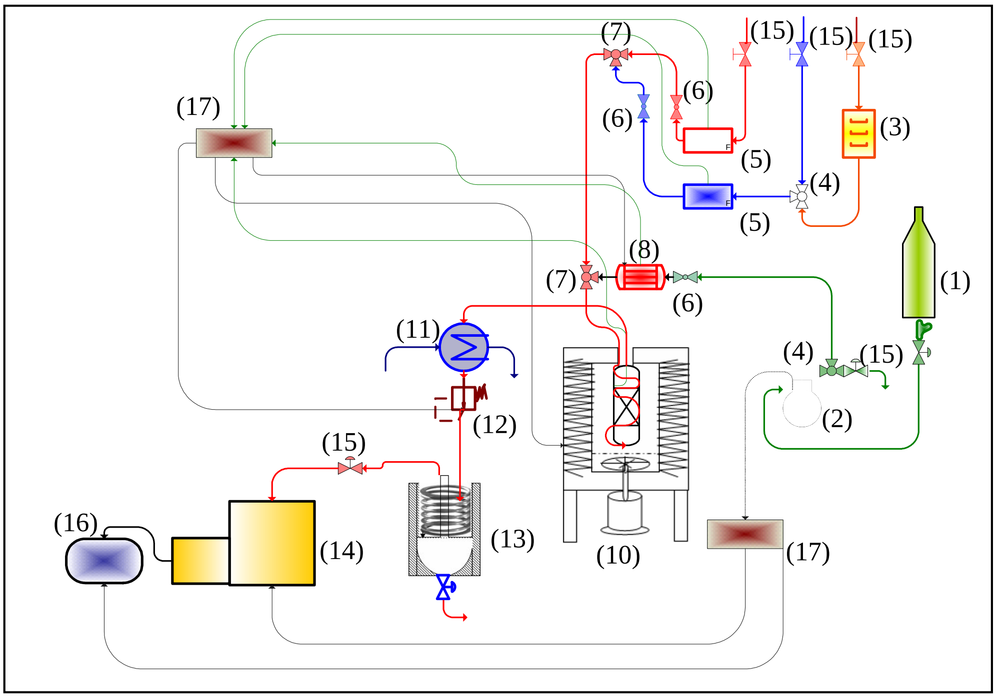

Fig.1: schematic flow diagram of catalytic experimant rig,
1-feeding tank, **2-** dosing pump, **3-** dryer, **4-** three way valve, **5-** mass flow meter for gases, **6-** one way valve, **7**-three way connection, **8-** evaporator, **9-** reactor, **10**-oven, **11**-heat exchanger, **12-** back pressure regulator, **13-** separator, **14-** gc, **15-** manual valve, **16**-pc, **17-** control and power supply box

3. RESULTS AND DISCUSSION

Surface area of prepared platinum zeolite catalysts were determined by nitrogen physisorption, (BET method). The data for surface area and other surface properties were taken directly by software that is interfaced with the device. The results of surface properties for original and noble metal loaded zeolite at different pressure and temperatures are listed in Table 1.

X-Ray diffraction was used to study the effect of modifications processes on the crystallinity and framework structure of Zeolite. Figures 2 and 3 exhibited the XRD patterns of zeolite HZSM-5 and HMOR respectively, when it's loaded by platinum. The shape and crystals of all samples were still the same without any change in spite of different percent of loading in addition to reduction process. The platinum should be appeared at 2θ=39.76, 46.24 and 67.45 [14] however the noise that appeared accompanied at these positions in addition to the low platinum concentration, therefore no lattice fringes were observed in the figure from most of the nanoparticles, presumably because of their small sizes and random orientations.

The morphology of the supported metal nanocomposites was characterized by Transmission Electron Microscopy (TEM). Figures 4 and 5, show the micrograph that taken by High Resolution TEM (HRTEM). The aggregation of platinum particles and slightly uniform distribution of particles was detected as for platinum loaded by impregnation method for each graph. The mean size of platinum particles was 8.847 and 6.893 nm for Pt/HZSM-5 and Pt/HMOR respectively

Table 1: bet surface area and pore volumes for different zeolite catalysts loaded with platinum

Sample name	BET surface area (m^2/g)	Area of pours (m^2/g)	Pore volume (cm^3/g)	Volume of pores (cm^3/g)	Pore size (A)
HMOR	539.2	117.6	0.157485	0.266646	90.725
Pt/HMOR	385.2	105.9	0.146832	0.245997	92.924
HZSM-5	403.7	195.3	0.076035	0.512954	105.057
Pt/HZSM-5	338.4	206.4	0.078006	0.525849	101.901

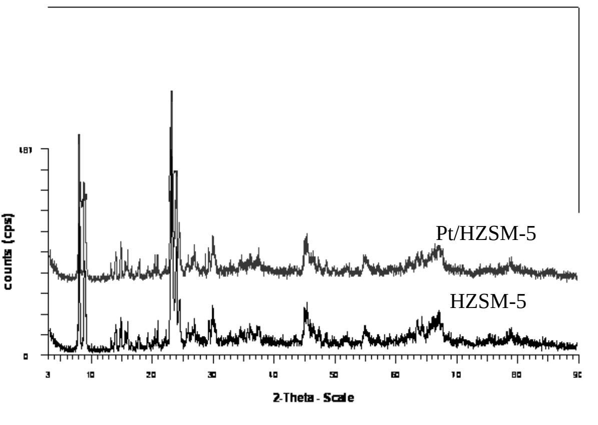

Fig. 2: XRD for original HZSM-5 and for Pt/HZSM-5 loaded by impregnation method

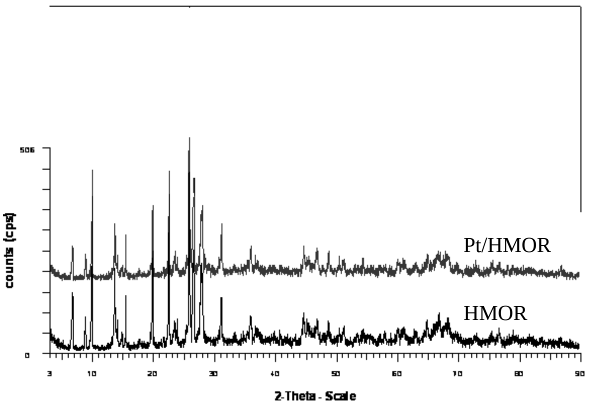

Fig. 3: XRD for original HMOR and for Pt/HMOR loaded by impregnation method

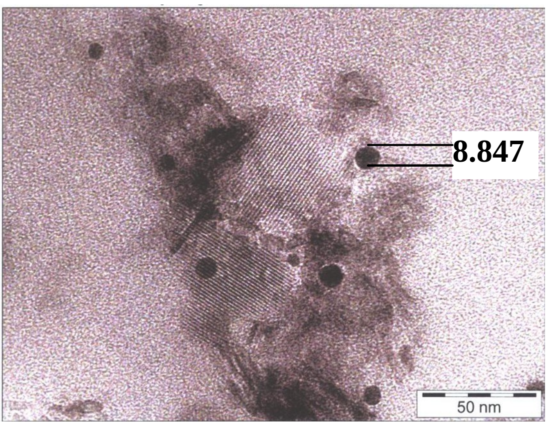

Fig. 4: TEM micrograph for Pt loaded Over HZSM-5 by impregnation method\

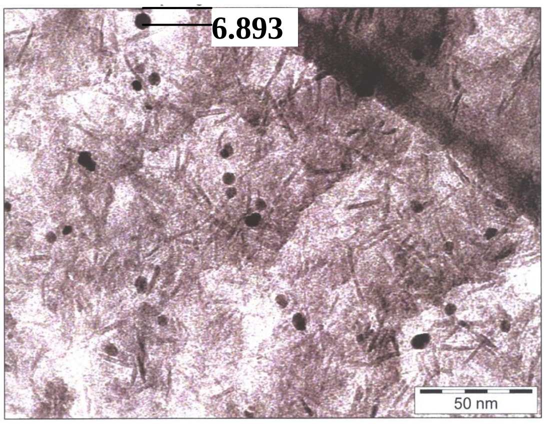

Fig. 4: TEM micrograph for Pt loaded Over HZSM-5 by impregnation method

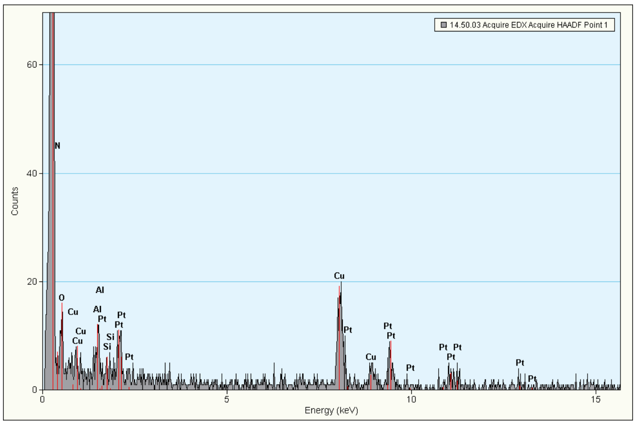

Fig. 6:EDXS for Pt/HZSM-5 loaded by impregnation

In order to obtain the chemical microanalysis for the same samples discussed in TEM analysis and due to the difficulty to analyze the crystal structure and shape of platinum, EDXS was used to character the platinum nanoparticles as shown in figure 6.

The spectrum contains strong characteristic Si, Al, C, O, and Pt X-ray peaks as expected, together with additional peak corresponding to Cu. This latter peak is an artifact that arises from the Cu grid on which the TEM sample is supported. Such fringes were, however, observed in occasional images, and one example is shown in the Figure 6 inset image. It shows a single nanoparticle with 1.3-Ǻ lattice fringes corresponding to the {111} planes of face-centered cubic metallic Pt. the individual Pt nanoparticles are defect-free single crystals.

The product distribution upon n-hexane isomerization is shown from tables 2 to 7. The fraction of C_1-C_4 cracked product, percent n-Hexane conversion, and catalytic selectivity towards isomerization as well as the isomers yield and aromatics yield were presented in these tables. The main important comparison between the prepared catalysts was selectivity and yield of desired product.

As it is expected that the temperature increase leads to conversion increase gradually. While the selectivity decreases with temperature increase. Temperature increase enhances the hydrocracking reactions producing more C_1-C_4 gases product, and decreasing the value of desired product. the selectivity of impregnated catalysts decrease rapidly, reaching about 20 % at 325 ^{o}C and 3 H_2/HC ratio as shown in the tables. Furthermore, the results show that Pt/HZSM-5 catalyst is more active and selective than Pt/HMOR catalyst for the considered temperature range.

The effect of hydrogen to hydrocarbon variation for n-Hexane isomerization reactions were carried out on Pt/HZSM-5 and Pt/HMOR catalysts. Both types were prepared by impregnation. All experiments were conducted at a constant flow rate of n-Hexane and H_2/HC ratios 3, 6 and 9 by increasing of hydrogen flow rate. It is noticed that a slightly increase in the selectivity is observed as H_2/HC ratio increased. This could be attributed to the fact that by increasing the hydrogen partial pressure the rate of cracking reactions is decreased. It was generally observed, that the conversion of n-Hexane increases gradually with increasing of H_2/HC ratio for all catalysts types and temperatures studied. This effect is noticeable at 325^{o}C as shown in the tables above.

The isomerization reaction of n-Hexane results usually in four isomers. Those are 2-Methylpentane (2MP), 3-Methylpentane (3MP), 2, 2-Dimethylbutane (2, 2 DMB) and 2, 3-Dimethylbutane (2, 3 DMB). 2MP and 3MP are the most required compounds for upgrading of motor gasoline, due to there sufficient volatility and high Octane number. Therefore, it was worthy to investigate the effectiveness of the platinum supported HZSM-5 and Mordenite catalysts towards the yield of these compounds. Special attention was done to the effect of loading method on the performance of catalysts. Furthermore, the hydrocracking of n-Hexane feed to C_1-C_4 hydrocarbons are considered as undesired reactions, producing gaseous components. The yield of C_1-C_4 fraction was also evaluated to study the catalytic behavior of platinum HZSM-5 and HMOR catalysts. Tables 2 to 7 shows that the yield of 2MP and 3MP on Pt/HZSM-5 and Pt/HMOR, respectively at different temperatures and H_2/HC ratios. Both catalysts were loaded by impregnation. The yields of 2MP and 3MP for catalysts

Pt/HZSM-5 are higher than for Pt/HMOR, because the former method gives uniform metal distribution on the support, resulted in more selective catalyst behavior. Furthermore, Pt/HZSM-5 shows more selective towards 2MP and 3MP than Pt/HMOR. Generally, the tables shown that, maximum yields for 2MP and 3MP were achieved at 275 ^{o}C within the temperature range 250-325 ^{o}C considered. The decline of yields by increasing the temperature is probably due to hydrocracking of these isomers, 2MP and 3MP to low hydrocarbons, mainly by using impregnated catalysts. Hydrogen to hydrocarbon ratio seems to be having a little effect on the yield of 2MP and 3MP for both catalysts. Generally, a ratio of about 6 shows as an optimum within the range studied.

Table 2: experimental results for isomerization of n-Hexane using Pt/HZSM-5 zeolite catalyst at *5 bar and H/HC=3*

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	3.35	0.42	0.22	27.67	20.47	47.65	0.22	52.35	93.18
275	13.38	0.07	1.65	35.19	26.07	23.41	0.23	76.59	82.23
300	29.61	0.23	2.11	27.06	21.11	19.56	0.32	80.44	62.79
325	68.67	0.91	4.43	5.89	7.35	12.14	0.61	87.86	21.15

Table 3: experimental results for isomerization of n-Hexane using Pt/HZSM-5 zeolite catalyst at *5 bar and H/HC=6*

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	3.12	0.31	0.28	34.09	26.18	35.78	0.24	64.22	94.76
275	10.71	0.42	1.05	36.72	28.04	22.82	0.24	77.18	85.81
300	26.08	0.99	1.16	31.47	22.47	17.64	0.19	82.36	68.10
325	61.92	1.27	5.81	12.19	8.17	10.46	0.18	89.54	30.65

Table 4: experimental results for isomerization of n-Hexane using Pt/HZSM-5 zeolite catalyst at ***5 bar and H/HC=9***

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	2.89	0.31	0.29	33.96	26.21	36.09	0.25	63.91	95.09
275	9.37	0.41	1.12	34.97	28.84	24.99	0.30	75.01	87.11
300	22.78	0.67	1.97	30.18	23.76	20.40	0.24	79.60	71.08
325	51.81	0.77	4.10	18.70	12.57	11.86	0.19	88.14	41.00

Table 5: experimental results for isomerization of n-Hexane using Pt/HMOR zeolite catalyst at ***5 bar and H/HC=3***

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	2.45	5.35	5.36	25.67	15.97	44.09	1.11	55.91	93.93
275	12.05	13.41	7.38	27.96	18.66	20.22	0.32	79.78	84.49
300	25.85	12.58	6.32	23.16	16.07	15.90	0.12	84.10	69.12
325	72.22	4.14	2.15	8.05	5.47	7.91	0.06	92.09	21.51

Table 6: experimental results for isomerization of n-Hexane using Pt/HMOR zeolite catalyst at ***5 bar and H/HC=6***

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	3.63	10.42	7.97	31.66	21.05	24.79	0.48	75.21	94.54
275	9.25	12.59	7.21	30.17	20.18	19.95	0.65	80.05	87.63
300	25.54	12.31	6.42	24.16	16.07	15.30	0.20	84.70	69.36
325	62.71	5.25	2.89	11.72	8.31	8.79	0.33	91.21	30.88

Table 7: experimental results for isomerization of n-Hexane using Pt/HMOR zeolite catalyst at ***5 bar and H/HC=9***

Temp.	(C1-C4)	2.2DMB	2.3DMB	2MP	3MP	n-C6	Aromatics	Conv. X%	Selec. S%
250	2.44	10.68	7.86	31.72	21.79	24.52	0.99	74.48	96.74
275	4.03	10.98	7.30	30.63	22.37	23.29	1.40	76.71	92.92
300	22.73	10.37	5.89	24.97	18.80	16.28	0.96	83.72	71.70
325	55.83	5.26	3.20	14.30	10.56	10.18	0.67	89.82	37.09

4. CONCLUSIONS

From the results it is obvious that the preparation of catalysts was not effected by treatment that was shown from the figures of XRD and the distributions of the particles is uniform but have aggregate form especially for Pt/HZSM-5 and have acceptable distribution for Pt/HMOR. The isomerization reaction is generally good for these types of catalysts where Pt/HZSM-5 is more active and selective than Pt/HMOR in addition the increasing of hydrogen to hydrocarbon ratio gave an increasing of selectivity, in summery the temperature between 270°C to 280 °C is more active and selective toward isomerization.

5. REFERENCES

[1] I.E. Maxwell, W.H.J. Stork, Stud. Surf. Sci. Catal. 58 (1991) 571–630.

[2] I.E. Maxwell, J.E. Naber, K.P. de Jong, Appl. Catal. A 113 (1994) 153–173.

[3] Editorial, Oil Gas J. 12 (1997) 21.

[4] R. Mijic, R. Micic, D. Comic, K. Djurdjevic, G. Boskovic, in: Proceedings of the First International Conference on Chemical Society of South-east European Countries, Halkidiki, Greece, June 1998, Book of Abstract, PO. 655.

[5] P.D. Hopkin, C.L. Marshall, J.T. Miller, L.B. Raska, in: J.W. Ward (Ed.), Catalysis 1987, Elsevier, Amsterdam, 1988, pp. 281–293.

[6] N.D. Triantafillou, J.T. Miller, B.C. Gates, J. Catal. 155 (1995) 131–140.

[7] G.S. Lane, F.S. Modica, J.T. Miller, J. Catal. 129 (1991) 145–158.

[8] I.I. Ivanova, M. Seirvert, A. Pasau-Claerbout, N. Blom, E.G. Derouane, J. Catal. 164 (1996) 347–362.

[9] M.M. Otten, M.J. Clayton, H.H. Lamb, J. Catal. 149 (1994) 211–222.

[10] Y. Hong, V. Gruver, J.J. Fripat, J. Catal. 150 (1994) 421–429.

[11] J. Abbot, B.W. Wojciechowski, Can. J. Chem. Eng. 66 (1988) 825–830.

[12] Z. Zhan, I. Manninger, Z. Paal, D. Barthomeuf, J. Catal. 147 (1994) 333–341.

[13] Y. Zhang, D. Kang, C. Saquing, M. Aindow and C. Erkey, *Ind. Eng. Chem. Res.*, 44, 4161, (2005).

[14] A. Bayrakceken, U. Kitkamthorn, M. Aindow and C. Erkey, *Scripta Materialia*, 56, 101, (2007).

تحسين الحفازات Pt/HZSM-5 و Pt/HMOR كحامل للحفاز البلاتيني

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الخلاصة

تم دراسة فعالية الحفازات ثنائية الاداء ، Pt/HZSM-5 و Pt/HMOR في ازمرة الهكسان الاعتيادي. تم تحظير الحفازات بطريقة التشريب ذي محتوى بلاتيني نحو ٠.٣ % حيث ان كلا الحفازين يتمتعان بحامضية عالية. يتمتع الحفاز نوع Pt/HZSM-5 بفعالية انتقائية اعلى باتجاه الازمرة اعلى من النوع Pt/HMOR. تم تشخيص ودراسة حبيبات البلاتين المحملة على نوعين الزيولايت بالطرق المعروفة Inductively Coupled) Plasma (ICP), X-Ray Diffraction (XRD), BET Surface Area, and Transmission (Electron Microscopy (TEM) فحص (TEM) يشير الى توزيع متجانس لحبيبات البلاتين على الحامل بمعدل قطر يتراوح بين ٦.٨٩٣ – ٨.٨٤٧ نانوميتر. كما تشير الفحوصات الى امكانية السيطرة على محتوى البلاتين وقطر الحبيبات بواسطة اختيار كمية معقد البلاتين المستخدم والظروف التشغيلية.